

Hooper

[45] **Date of Patent:** Mar. 13, 1990

Attorney, Agent, or Firm—The Dulin Law Firm

12 Claims, 3 Drawing Sheets

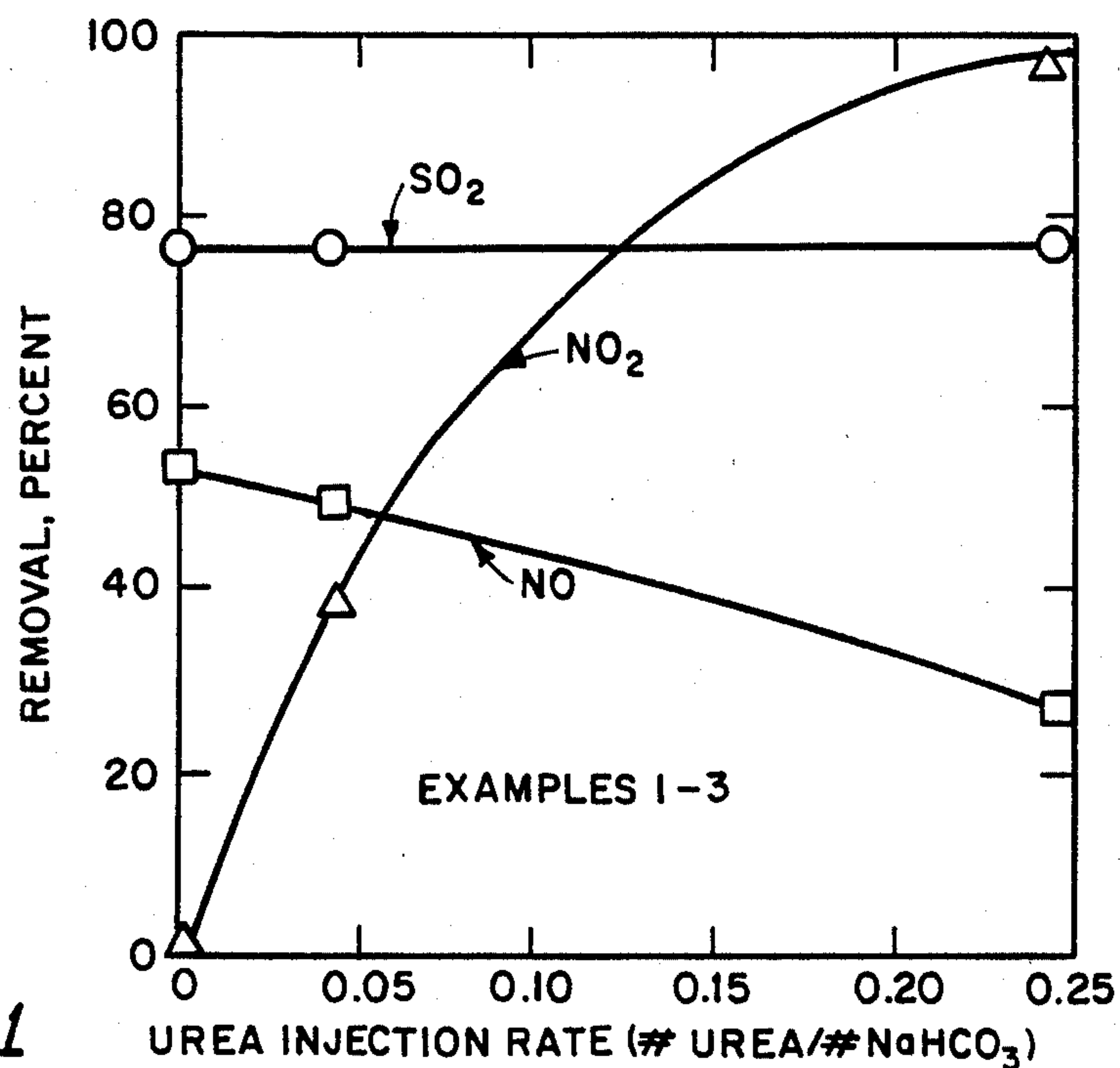


Fig. 1

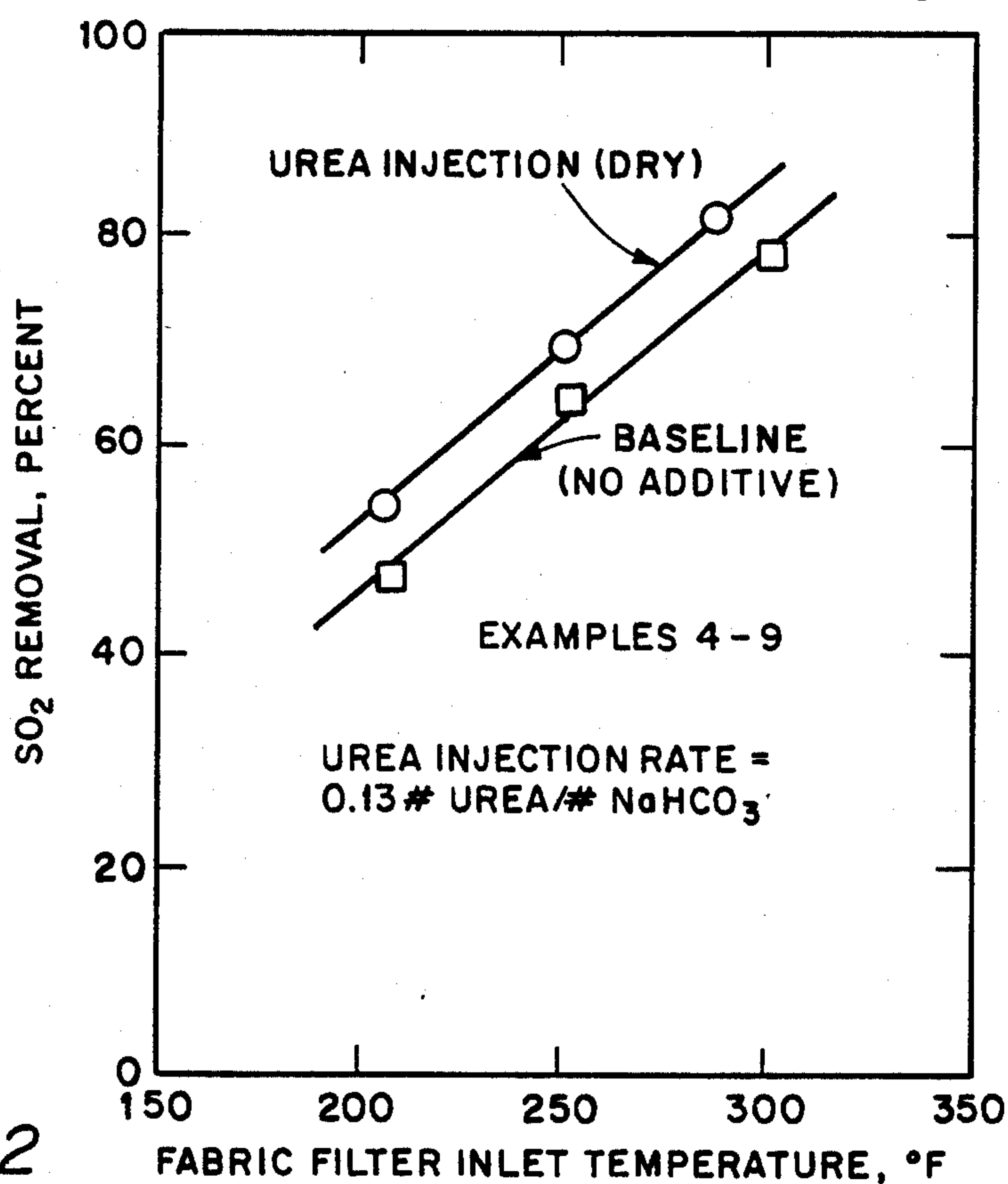


Fig. 2

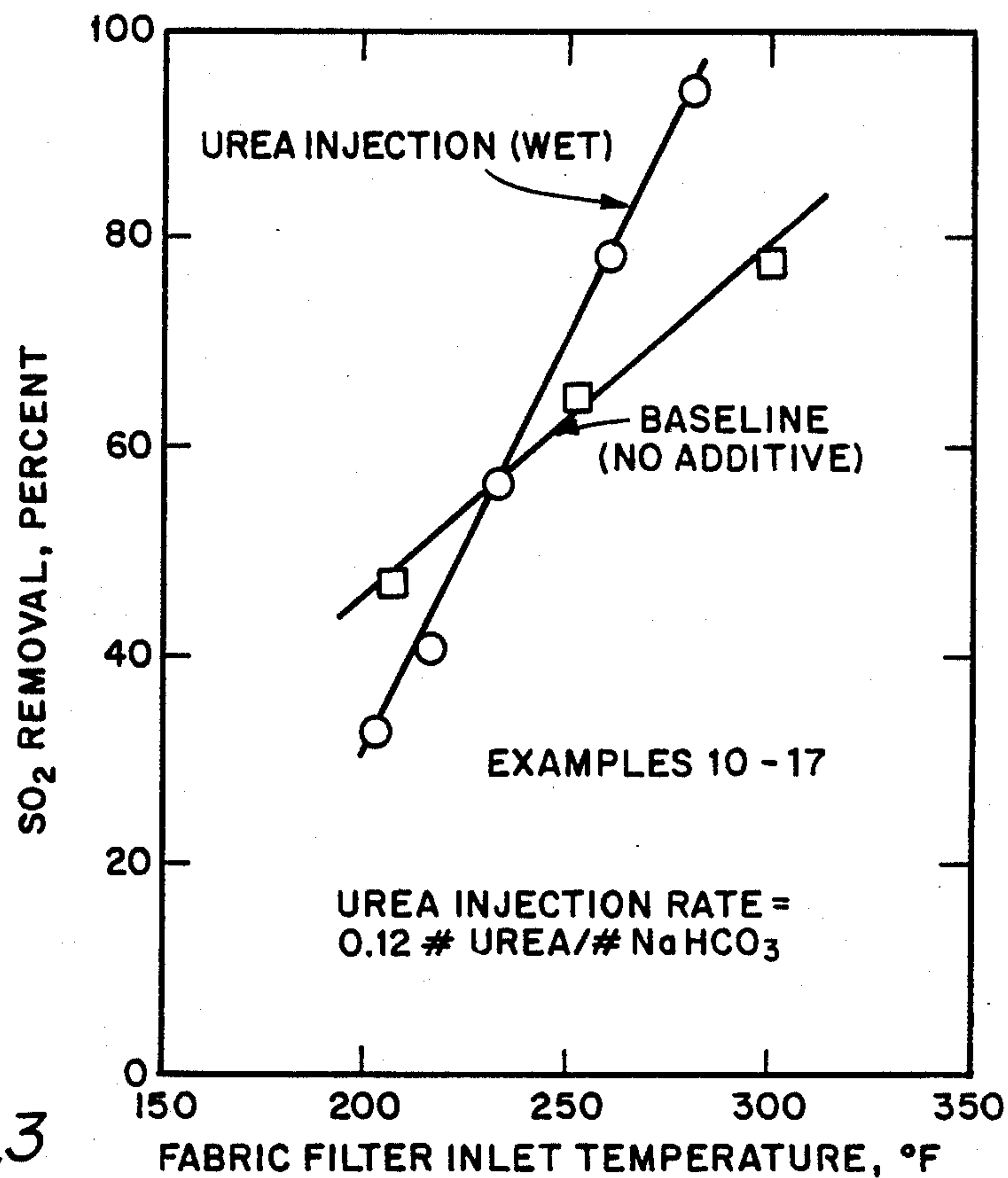


Fig. 3

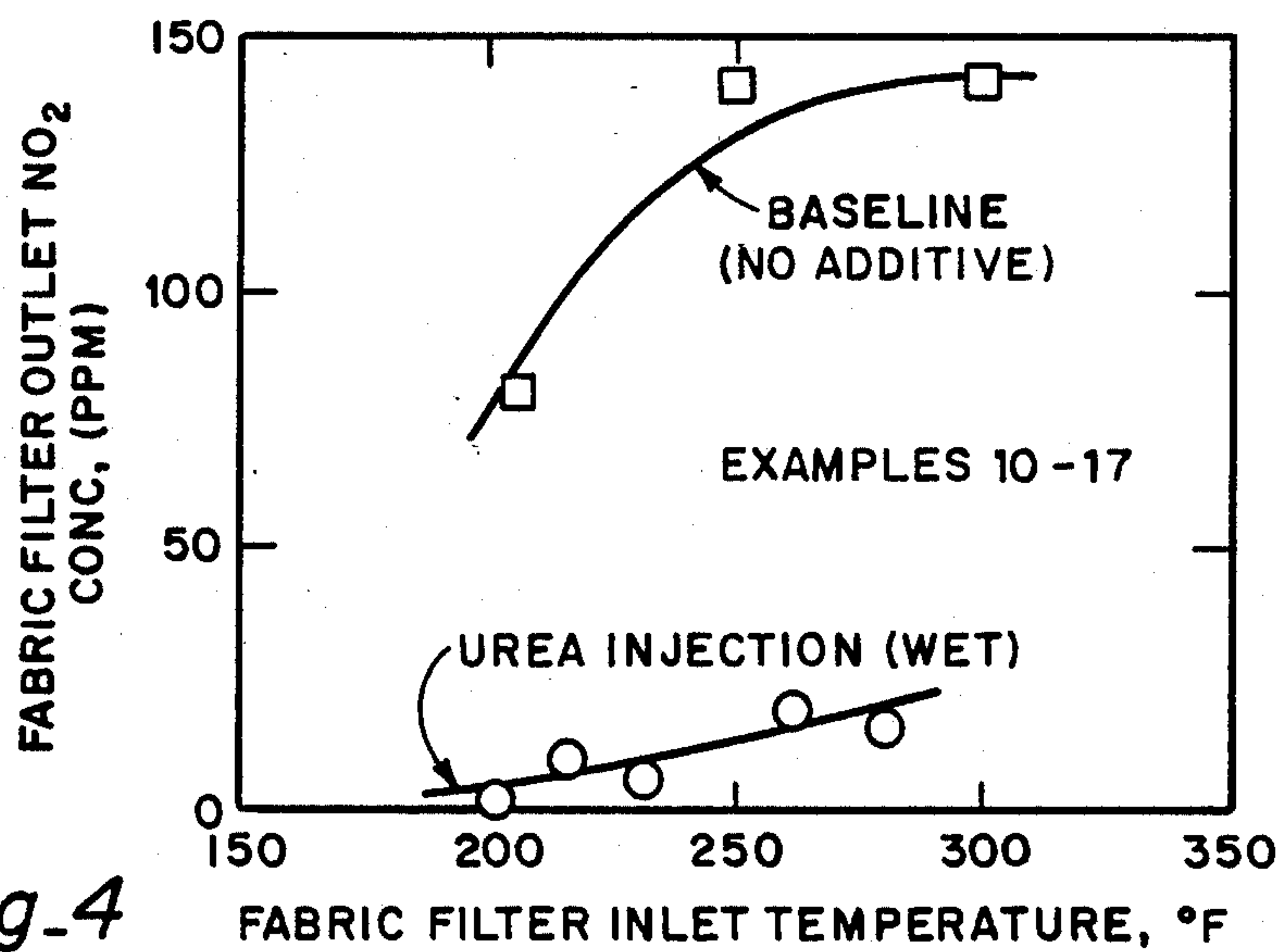
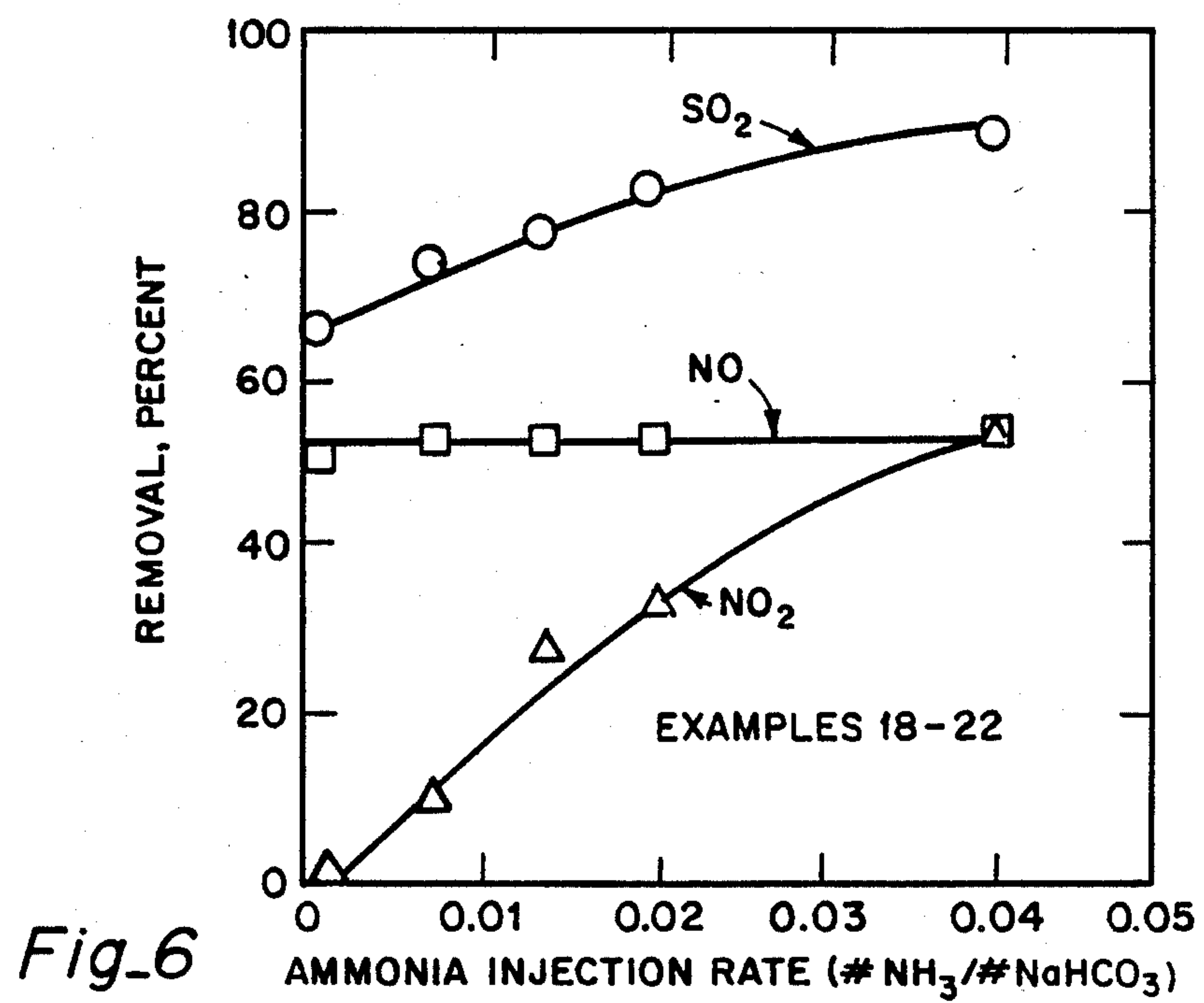
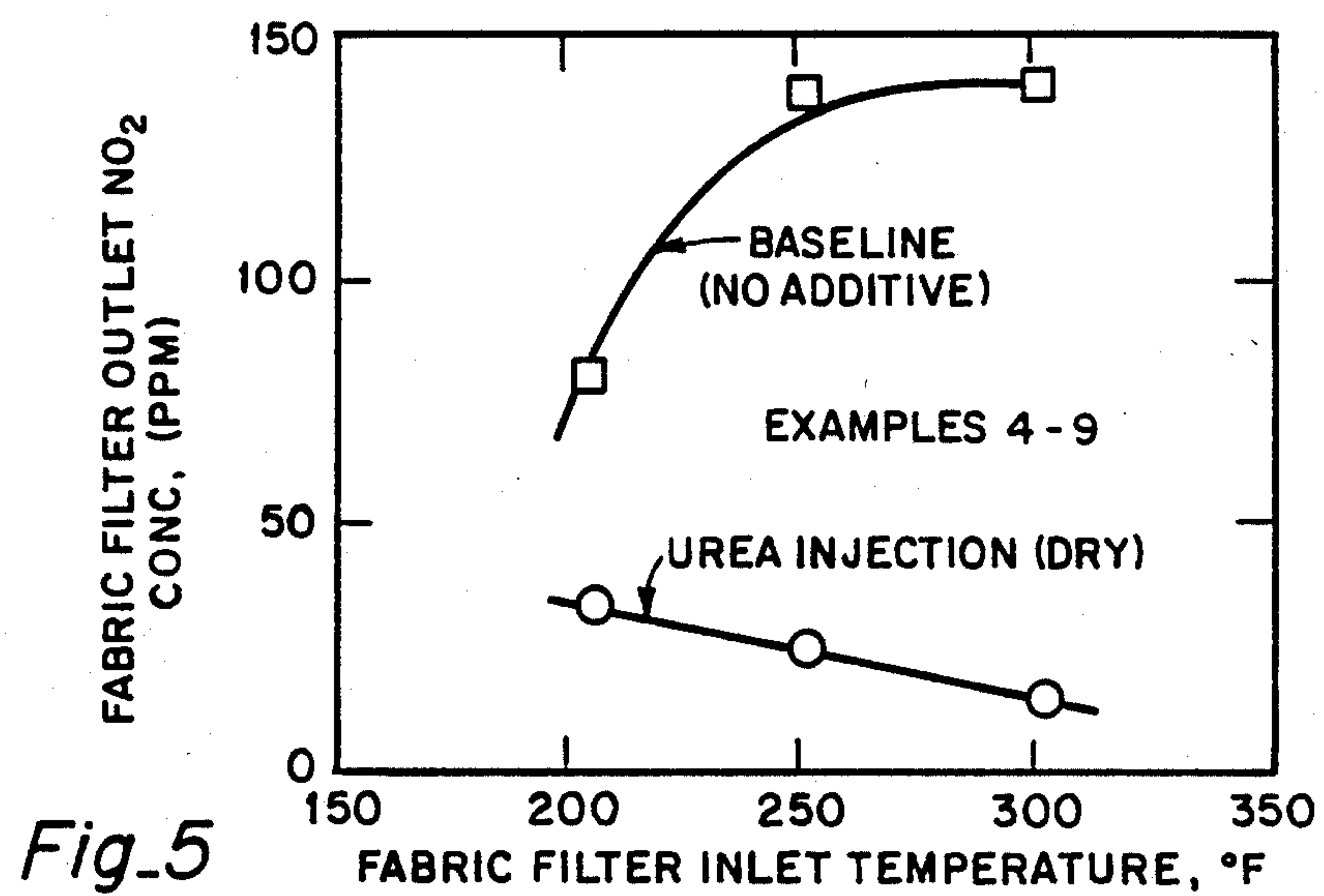


Fig. 4



METHOD FOR BAGHOUSE BROWN PLUME POLLUTION CONTROL

FIELD

The invention relates broadly to a method for baghouse SO_x/NO_x pollution control, and more specifically to a method for control of brown plume coloration associated with the injection of sodium reagents into the flue gas duct work ahead of a baghouse to remove SO_2 from industrial and utility plants that fire (burn) fossil fuels or wastes to generate electricity, steam or heat. More particularly, the method of the invention employs sodium bicarbonate (preferably nahcolite) plus urea or ammonia to suppress the formation of NO_2 which causes plume coloration in exit flue gases.

BACKGROUND

The increasing use of sulfur-containing fuels as energy sources, namely coal and oil, has resulted in pollution of the atmosphere throughout the world. The burning of the fuel produces flue gases containing substantial quantities of SO_x , predominantly SO_2 and SO_3 .

A wide variety of processes have been proposed for the removal of the SO_2 from flue gases before they are emitted to the atmosphere. Processes using dry solids, liquids or slurries of sorbents injected in a manner to directly contact the flue gases have proven to be effective for control of SO_2 emissions. Of these, the calcium-based wet scrubber systems have experienced the greatest use in industrial and utility application. This involves finely grinding lime or limestone of suitable composition, forming a water slurry or mixture, and providing apparatus and method for slurry contact with the flue gases. The SO_2 reacts with the calcium reagent to form calcium sulfate/sulfite which is collected and removed in the form of a generally thixotropic sludge. This sludge is usually difficult to dispose because it does not easily dewater, and heavy metals can leach from the waste sludge containment ponds.

Further, abrasion to the slurry pumps and other scrubber handling equipment (due to the hardness of the limestone particles) increases maintenance costs. The operating costs are increased because the evaporation of water in the system cools the flue gases nominally by 200°F . The moist flue gases, containing as they do some residual dissolved SO_x , are also acidic. In addition, where the utility or industrial plant is located in an arid region, the water requirements of a wet pollution control process are expensive and drain an already scarce natural resource.

The subject of flue gas desulfurization by the injection of dry sodium-based reagents has been extensively investigated in laboratory, pilot, and full scale applications since the 1960's. These investigations have provided the technical basis to evaluate the economic aspects of the technology and compare its advantage to the current calcium-based technologies. The injection of dry reagents clearly is the least demanding of capital funds for both new and retrofit applications. The use of familiar hardware such as pulverizers, blowers, and silos permit the easy installation and operation of this simple technology.

Accordingly, the injection of dry reagents into flue gases have become of increasing interest. Principal among these is the use of sodium compounds as a reagent or sorbent. Sodium-based reagents that have been used are commercial sodium bicarbonate (NaHCO_3),

light and dense soda ash (Na_2CO_3), sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), trona (a naturally occurring form of sodium sesquicarbonate), and Nahcolite (a naturally occurring form of sodium bicarbonate).

The reagents of greatest effectiveness are commercial sodium bicarbonate and Nahcolite. The sodium bicarbonate or Nahcolite is injected into the flue gas duct of a utility or industrial plant, and reacts with SO_2 in the gas stream to produce Na_2SO_4 which is collected in a baghouse or on plates of an ESP.

However, I have observed that the use of sodium can result in production of a reddish-brown plume coloration in stack gases downstream of the particulate control device. The use of the sodium bicarbonate not only removes SO_2 , but also removes some NO_x (NO and NO_2). While the precise mechanism is not known at this time, it is presently thought that some step within the overall sulfation reaction (reaction of sodium reagent with SO_x) initiates the oxidation of NO to NO_2 . It is the presence of the NO_2 in the exiting flue gases which is the source of the plume coloration.

Accordingly, this promising sodium reagent SO_x control process has a serious disadvantage, in that its use creates an NO_2 plume in the process of its removal of SO_x pollution from flue gases. Accordingly, there is a great need for a method by which the NO_2 produced by the use of sodium reagents can also be removed or suppressed, while not sacrificing SO_x removal. This invention permits the injection of dry sodium reagents ahead of a baghouse without production of the plume.

THE INVENTION

Objects

It is among the objects of this invention to provide a method for removal or suppression of NO_2 formation during the injection of dry sodium reagents ahead of a baghouse, particularly injection of sodium carbonate/bicarbonate compounds into flue gases of utility and industrial plants ahead of a baghouse for removal of SO_x .

It is another object of this invention to provide a method for use of urea and/or ammonia in conjunction with dry sodium reagents in a baghouse process for suppression of formation of NO_2 while simultaneously removing SO_x .

It is another object of this invention to provide a method of NO_2 removal or suppression by introduction of urea or ammonia in combination with a sodium bicarbonate reagent into the flue gas of such plants ahead of a baghouse.

It is another object of this invention to improve the SO_x removal efficiency of sodium-based reagents in a baghouse pollution control process, particularly sodium bicarbonate/Nahcolite, while at the same time removing NO_x and suppressing NO_2 emissions to the atmosphere.

Still other objects of this invention will be evident from the Summary, Drawings, Detailed Description, Abstract and Claims of this case.

SUMMARY

The method of this invention comprises the introduction of sodium bicarbonate, preferably commercial sodium bicarbonate or Nahcolite (either or both herein termed "bicarb"), in a finely divided dry form, into the flue gas of a utility or industrial plant ahead of a baghouse in the range of from about 0.1 to 1.5 the Normal-

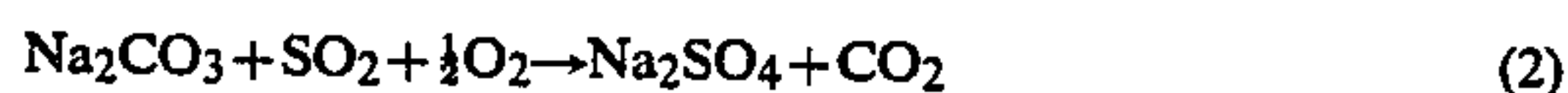
ized Stoichiometric Ratio of the SO_x to be removed, along with the separate but simultaneous injection of an additive selected from urea and/or ammonia in the range of from about 1 to 25% by weight urea to the weight of the bicarb. The amount of urea injected is preferably about 5 to 15%, while the ammonia is from 1-5%. The additive may be introduced in either dry or liquid form, e.g., a crystalline powder or concentrated solution in water, and both the additive and reagent are injected evenly throughout the gas stream ahead of the baghouse. The reaction products collected by the baghouse can be disposed in the same manner as sodium reagents used without the use of urea or ammonia additive.

While I do not wish to be bound by theory, I presently believe the reaction of the oxides of sulfur (SO_2 , SO_3) with NaN (CO_3), the product of the thermal decomposition of Nahcolite or sodium bicarbonate (NaHCO_3). Therefore, when sodium bicarbonate/Nahcolite (herein bicarb) is injected, the first step necessary for SO_2 removal is the decomposition into sodium carbonate:



The rate of the decomposition of the bicarb controls the distance downstream of the injection location where the SO_2 reaction begins, and, generally speaking, the temperature of the particular flue gas at the injection location determines the rate of decomposition. Other factors influencing decomposition rate include coal type, fly ash composition, and CO_2 , NO and humidity in the flue gas.

Once the decomposition has proceeded sufficiently to provide sites of sodium carbonate, the SO_2 then rapidly reacts according the following overall reaction:



In the process, there is some conversion of nitrogen oxide (NO) to nitrogen dioxide (NO_2). Some, but not all of the NO_2 reacts with the carbonates and/or sulfates produced by the injection of the reagent. The remaining unreacted NO_2 exits the baghouse and is responsible for producing a reddish-brown plume coloration. This plume coloration problem arose when NO_2 exceeds about 30 ppm (not corrected to 0% O_2) under the baghouse conditions of this pilot test. Surprisingly, the use of urea or ammonia along with the bicarb reagent reduces or eliminates the unreacted NO_2 from the exit gas stream and thereby prevents the unwanted plume coloration.

The two additives were tested in two ways: First, in a bench scale 0.2 ACFM fluidized bed of commercial sodium bicarbonate (Church & Dwight 3DF), where a simulated flue gas is used to fluidize an inch deep bed of the sodium bicarbonate. These tests were used as a pre-screening to determine if larger scale testing was warranted. The results showed that both additives merited further test work. Since the fluid bed test work was small scale for pre-screening, those tests are not reported here. Only the more significant, best mode pilot baghouse scale tests are reported herein.

Second, a pilot scale baghouse test series used a 2200 ACFM slip stream of gases from a coal-fired power plant, with the exhaust gases downstream of the pilot-sized baghouse being returned to the main gas stream ahead of the regular plant baghouse. The flue gases slip stream was withdrawn in the range of 260°-275° F., and

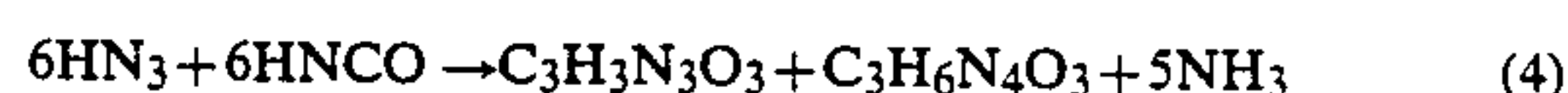
heated to test conditions, typically 300° F. Urea was tested in the range of 205° F. (wet injection) to 330° F. (dry injected). Typical stack O_2 was around 6%.

Fluid bed testing of ammonia, however, was not as encouraging as that for urea. Extremely high levels of ammonia (~5:1) were necessary in the fluid bed reactor to obtain significant NO_2 removal. However, ammonia proved to be much more effective in reducing NO_2 concentrations in the pilot plant baghouse system than it did in the bench reactor. Although the NO_2 reduction mechanism with NH_3 is significantly different than with urea, the two compounds appear about equally effective in reducing NO_2 on a moles of nitrogen injected basis.

When urea is heated above its melting point (271° F.), it decomposes into ammonia and isocyanic acid by the equilibrium:



These compounds may then polymerize into a mixture of cyanuric acid, triuret, and ammonia by the following equilibrium:



Because of the variety of forms which may be encountered when urea decomposes under variable conditions, it is currently unknown just what compound was active during this testing.

During the preliminary fluid bed tests of the urea additive, it appeared to be effective at temperatures fifty degrees lower than the referenced melting temperature. Further, the urea additive appeared to aid in low temperature decomposition of the sodium bicarbonate sorbent. The mass mean diameter of the sodium bicarbonate was about 100 μm (micrometers).

DRAWINGS

The invention is further illustrated in connection with the drawings in which:

FIG. 1 is a graph showing the effects of urea addition when injecting sodium bicarbonate for flue gas desulfurization in terms of removal percent of SO_2 , NO and NO_2 vs. urea injection rate (lbs. urea/lb. NaHCO_3) at 300° F.

FIG. 2 is a graph showing the effects of dry urea addition and temperature on SO_2 removal when injecting sodium bicarbonate for flue gas desulfurization in terms of SO_2 removal percent vs. fabric filter (baghouse) inlet temperature, at 13% dry urea injection rate.

FIG. 3 is a graph showing the effects of wet urea addition and temperature on SO_2 removal when injecting sodium bicarbonate for flue gas desulfurization in terms of SO_2 removal percent vs. fabric filter (baghouse) inlet temperature, at 12% wet urea injection rate.

FIG. 4 is a graph showing the effects of wet urea addition and temperature on outlet NO_2 concentration when injecting sodium bicarbonate for flue gas desulfurization in terms of fabric filter (baghouse) outlet concentration (in ppm) vs. fabric filter (baghouse) outlet temperature in °F. for wet urea injection.

FIG. 5 is a graph showing the effects of dry urea addition and temperature on outlet NO_2 concentration when injecting sodium bicarbonate for flue gas desulfurization in terms of fabric filter (baghouse) outlet

NO₂ concentration (in ppm) vs. fabric filter (baghouse) inlet temperature in °F. for dry urea injection.

FIG. 6 is a graph showing the effects of from 1–5% ammonia addition when injecting sodium bicarbonate for flue gas desulfurization in terms of removal percent of SO₂, NO and NO₂ vs. ammonia injection rate in the range of 1–5% (lbs. NH₃ per lb. NaHCO₃).

DETAILED DESCRIPTION OF THE BEST MODE—EXAMPLES 1–22

The following detailed description illustrates the invention by way of example, not by way of limitation of the principles of the invention. This description will clearly enable one skilled in the art to make and use the invention, and describes several embodiments, adaptations, variations, alternatives and uses of the invention, including what I presently believe is the best mode of carrying out the invention.

While the terms sodium bicarbonate and Nahcolite are used interchangeably throughout in case of generic descriptive context, the tested reagent (or sorbent) was commercial sodium bicarbonate. The term "reagent" means the sodium reagent alone, while "additive" means ammonia or urea. The test results are shown as the data points on the graphs of FIGS. 1–6 as the simplest, most direct way of recording the data and illustrating the relationship observed.

TEST SET-UP

The fluid bed test set-up was a 0.2 ACFM stream of simulated flue gases passing through a 1" high heated bed of sodium bicarbonate in a reactor chamber comprising a sintered glass plate spanning a vertical 1" diameter glass tube. The gases were heated to the test temperature by external heaters and fed upwardly through the plate to fluidize the bed. The dry additive was injected by a small feeder into the bed when fluidized. The wet additive solution was sprayed into the reactor at the same level. A static filter was used downstream to catch blow-by from the bed. The simulated flue gases contained: 12% CO₂; 6% O₂; 900 ppm SO₂; 0% NO₂; balance N₂; and the NO varied from test to test in the range of 400–900 ppm.

The pilot test series baghouse set-up comprised of tapping off a 2200 ACFM slip stream of flue gases from a coal-fired power plant burning a typical western sub-bituminous coal ranging from about 10,500 BTU/lb to 12,800 BTU/lb, 8% ash, and 0.3–0.5% S. The 12" duct was insulated and heated to maintain the flue gas at the desired test temperature in the main duct. A small feeder placed some 10' upstream of a pilot baghouse (24 bags, each 9" diameter by 12' long, vertically hung, bottom entry) was used to introduce the dry sodium bicarbonate reagent. This provided about 0.1 sec gas stream residence time for the reagent and additive. Additional time for reaction is provided by the residence time of the reagent and additive collected on the bag cake. For the additive injection, a second small feeder (for dry additive), or spray nozzle (for wet additive) was positioned in the same location. The cleaned flue gases exiting the pilot bag were reintroduced into the main gas stream. Plume formation or reduction was not directly observed. Rather, it was inferred from NO₂ concentration measurements on the outlet side of the pilot baghouse.

Inlet temperatures and SO₂, NO and NO₂ concentrations were taken ahead of the reagent and additive in-

jection point, and outlet just downstream of the filter media.

Sulfur dioxide (SO₂), nitrogen oxide (NO), total oxides of nitrogen (NO_x), Oxygen (O₂), carbon dioxide (CO₂), and nitrogen dioxide (NO₂) were continuously sampled, monitored and recorded on analog strip charts. Calibration was conducted several times daily with standard bottled calibration gases. SO₂, NO or NO_x, and O₂ were measured for selected periods at one location and then switched to the other location for selected periods.

The continuous monitoring system used the analytical instruments as described below:

Flue Gas Component	Measurement Method
Sulfur Dioxide	Ultraviolet, photometric
Nitrogen Dioxide	Chemiluminescence
Nitrogen Oxides	Electrochemical
Oxygen	NDIR*, photometric
Carbon Dioxide	

*NDIR means Non-Destructive Infrared

Using these monitors, samples of flue gas were withdrawn through stainless steel, sintered filters and heated sample lines and analyzed for concentrations of SO₂, NO, NO_x, NO₂, CO₂, and O₂.

PILOT BAGHOUSE TEST RESULTS

FIG. 1 presents SO₂, NO and NO₂ removals for Examples 1–3, a comparative test series for dry injection of urea. Example 1 is the base line case of no urea additive (data points on the left of each line on the graph). Example 2 shows 5% urea addition (central three data points), and Example 3 shows 25% urea addition (data points at the right end of each line on the graph). Nominal conditions during testing were the following:

Fabric filter inlet temperature	=	300° F.
Fabric filter inlet SO ₂ /NO ratio	=	1.25
Fabric filter inlet SO ₂ concentration	=	900 ppm
NaHCO ₃ to SO ₂ NSR*	=	1.0

*Normalized Stoichiometric Ratio

Inspection of FIG. 1 reveals no effect of urea injection on SO₂ removal but a significant effect on NO and NO₂ emissions. The rapid increase in NO₂ removal with injection rate is accompanied by a drop in NO removal. Urea apparently works to reduce NO₂ emissions by interfering with the NO and NO₂ oxidation step discussed previously. The result is a drop in NO removal and associated NO₂ emissions.

FIG. 2 shows data points for Examples 4–9 (each point being a test example), which are graphed as SO₂ removal as a function of fabric filter inlet temperature. The data was obtained with a constant dry urea injection rate of 0.13 lbs. of urea per pound of sodium bicarbonate injected. A definite improvement in SO₂ removal over baseline conditions is observed, especially at lower temperatures.

For Examples 10–17 FIG. 3 presents pilot baghouse test data, similar to that shown in FIG. 2, except the urea additive is injected as a solution at a 12% rate. Lower SO₂ removals (below baseline) seen in the figure at lower temperatures appear to be the result of poor atomization and evaporation of the urea C solution. Increased SO₂ removals at higher temperatures may be

the result of improved evaporation and dispersion of the additive droplets.

FIGS. 4 and 5 present NO₂ pilot baghouse test data from Examples 10-17 (FIG. 4) and Examples 4-9 (FIG. 5) for fabric filter outlet NO₂ emissions as a function of inlet temperature and form (wet or dry) of additive injection. The data indicate better NO₂ removals at low temperatures by the concentrated urea solution as compared to dry injection of the additive. The cause of this result could once again be related to some artifact of the injection/evaporation process, or simply be due to data scatter.

AMMONIA ADDITIVE RESULTS

A series of tests (Examples 18-22) to evaluate injection of a concentrated aqueous solution of pure anhydrous ammonia as an NO₂ mitigation additive were conducted at essentially the same conditions as for the pilot scale baghouse tests of urea. Data from this series is presented in FIG. 6. As seen from inspection of the figure, significant NO₂ capture is possible with ammonia.

A significant increase in SO₂ removal was also observed whenever ammonia was injected into the gas stream. A gas phase reaction between ammonia and sulfur dioxide at the temperatures tested was somewhat surprising, giving rise to questions concerning potential problems with the sampling system. SO₂ removal data was, however, obtained using two separate continuous monitoring systems. One monitor operating dry employed an upstream condenser sample-conditioning system. Another monitor, however, analyzed a hot, wet gas sample at a temperature consistent with that encountered in the flue gas stream.

It appears that the SO₂ removal with ammonia may be by some process other than a gas phase reaction. Other research at Arapahoe reported in *Selective Catalytic Reduction for Coal-Fired Power Plants—Pilot Plant Results*, Palo Alto, Calif.; Electric Power Research Institute, April 1986. CS-4386, has indicated reaction of SO_x and ammonia in the gas stream with aluminum in the fly ash. This may result in formation of an ammonium/aluminum/sulfate compound with the net effect of increasing SO₂ removal.

DISCUSSION

Urea and ammonia both appear to be useful additives for NO₂ control where sodium bicarbonate injection in a baghouse system is used for SO₂ reduction. The advantage of urea is to prevent NO₂ formation while increasing NaHCO₃ reactivity down to 210° F. NO₂ formation is sensitive to BET surface area of bicarb; i.e., the greater the BET the greater NO₂ formation.

As an alternative to sequential or simultaneous urea or ammonia injection up or downstream of the reagent injection point, the following process steps may be employed:

- injection of bicarb at 550° F.-700° F. in the duct just before the air preheater, or take a slip stream and inject the bicarb. At this temperature, no NO₂ is formed;
- then inject NH₃ downstream of the air preheater. This will reduce 50% of the usual NO₂ formation while some NH₃ will react with SO₂; and
- then inject urea, H₂NCONH₂. This has a higher NO₂ reduction capability than NH₃, so it can eliminate NO₂ formation and increase SO₂ removal by bicarb at lower temperatures.

It should be understood that various modifications within the scope of this invention can be made by one of ordinary skill in the art without departing from the spirit thereof. I therefore with my invention to be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.

I claim:

1. An SO_x/NO_x air pollution control process employing a baghouse to simultaneously control particulate emissions comprising the steps of:

- introducing a sodium-based reagent into a stream of flue gas containing SO_x and NO_x, said flue gas having a temperature above about 200° F.;
- introducing urea as an additive into said flue gases in an amount ranging from about 1 to about 25% by weight of said sodium-based reagent;
- maintaining said reagent and said additive in contact with said flue gas for a time sufficient to react said reagent with some of said SO_x and NO_x thereby reducing the concentration of said SO_x and NO_x in said flue gas;
- said additive, as compared to use of said reagent without said additive, increasing the percent SO_x removal and the percent NO_x removal by said reagent while suppressing conversion of NO to NO₂ by said reagent to below about the visible brown plume threshold; and
- collecting said reacted reagent and additive in a baghouse.

2. An SO_x/NO_x air pollution control process as in claim 1 wherein said sodium-based reagent is selected from the group consisting essentially of sodium bicarbonate, Nahcolite, soda ash, trona, carbonated trona, sodium sesquicarbonate, and combinations thereof.

3. An SO_x/NO_x air pollution control process as in claim 2 wherein said reagent is selected from the group consisting essentially of dry Nahcolite and sodium bicarbonate.

4. An SO_x/NO_x air pollution control process as in claim 3 wherein said additive is urea.

5. An SO_x/NO_x air pollution control process as in claim 4 wherein:

- said reagent introduction step includes feeding said reagent in a dry, finely divided condition from a first hopper at a metered rate in relation to a predetermined amount of SO_x reduction desired; and
- said urea introduction step includes feeding said urea in a dry crystalline form from a second hopper at a rate within said 1 to 25% by weight range in relation to a predetermined NO₂ removal percent desired.

6. An SO_x/NO_x air pollution control process as in claim 4 wherein:

- said reagent introduction step includes feeding said reagent in a dry finely divided condition into the flue gas to be treated from a hopper at a metered rate in relation to a predetermined amount of SO_x reduction desired; and
- said urea introduction step includes spraying said urea in a solution form into the flue gas to be treated at a rate within said 1 to 25% by weight range in relation to a predetermined NO₂ removal percent desired.

7. An SO_x/NO_x air pollution control process as in claim 3 wherein said urea is used in an amount of from about 5% to 25% of said reagent.

8. An SO_x/NO_x air pollution control process as in claim 7 wherein:

- (a) said reagent introduction step includes feeding said reagent in a dry, finely divided condition from a first hopper at a metered rate in relation to a predetermined amount of SO_x reduction desired; and
- (b) said urea introduction step includes feeding said urea in a dry crystalline form from a second hopper at a rate within said 1 to 25% by weight range in relation to a predetermined NO_2 removal percent desired.

9. An SO_x/NO_x air pollution control process as in claim 1 wherein said urea is used in an amount of from about 5% to 25% of said reagent.

10. An SO_x/NO_x air pollution control process as in claim 9 wherein:

- (a) said reagent introduction step includes feeding said reagent in a dry, finely divided condition from a first hopper at a metered rate in relation to a predetermined amount of SO_x reduction desired; and
- (b) said urea introduction step includes feeding said urea in a dry crystalline form from a second hopper at a rate within said 1 to 25% by weight range in

relation to a predetermined NO_2 removal percent desired.

11. An SO_x/NO_x air pollution control process as in claim 13 wherein:

- (a) said reagent introduction step includes feeding said reagent in a dry, finely divided condition into the flue gas to be treated from a hopper at a metered rate in relation to a predetermined amount of SO_x reduction desired; and
- (b) said urea introduction step includes spraying said urea in a solution form into the flue gas to be treated at a rate within said 1 to 25% by weight range in relation to a predetermined NO_2 removal percent desired.

12. An SO_x/NO_x air pollution control process as in claim 4 wherein:

- (a) said reagent introduction step includes feeding said reagent in a dry finely divided condition into the flue gas to be treated from a hopper at a metered rate in relation to a predetermined amount of SO_x reduction desired; and
- (b) said additive injection steps include spraying concentrated aqueous solutions of said additive into said flue gases.

* * * * *

30

35

40

45

50

55

60

65